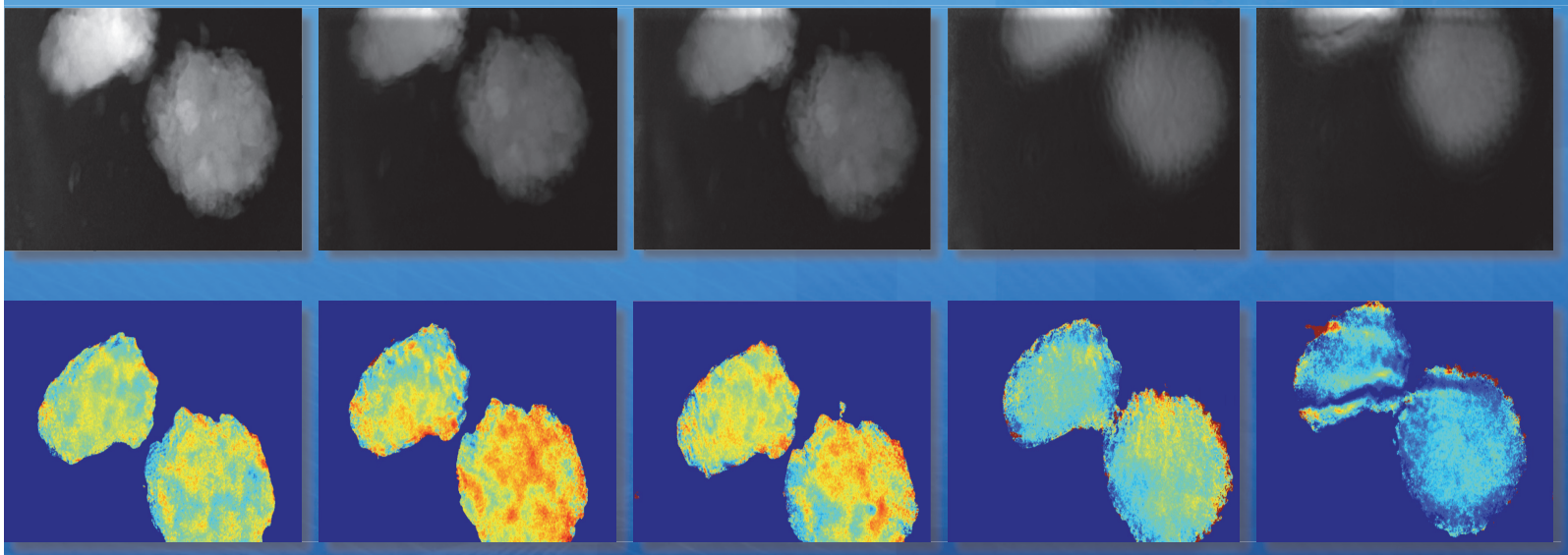


# Interfacial Studies of Emerging Cathode Materials

Marca M. Doeff
Lawrence Berkeley National Laboratory
June 11, 2019

Project ID # BAT408

# Overview

## Timeline

- Project start date 10/1/2018
- Project end date 9/30/2021
- Percent complete 12.5%

## Budget

- Total project funding
  - DOE share 100%
  - Contractor share N/A
- Funding for FY 2019 $300k

## Barriers

- Barriers addressed
  - Energy Density
  - Cost
  - Cycle Life
  - Safety

## Partners

- LBNL, SSRL, VA Tech
- Project lead: LBNL

# Relevance

- The thermal instability of (partially) delithiated Ni-rich NMCs is an impediment to their use in EV batteries because of safety concerns. Note that high temperatures can be reached in cells under abuse conditions (thermal runaway). Understanding the thermal behavior of Ni-rich NMCs is critical. (FY2018 project).
- To reach energy density and cost goals, high capacity cathode materials with significant O redox capacity should be considered (FY2019 project).
- Little is currently known about the interfacial reactivity of these materials or their impact on safety and cyclability.
- We propose to investigate the interfacial properties of candidate O-redox materials using surface and bulk sensitive techniques we have developed for NMC materials in our previous project.

# Milestones-Last half of 2018*

| Milestone | Type | Date/Status |
|---|---|---|
| Complete surface characterization of pristine and cycled NMC-811 | milestone | Q3/completed |
| Go/no go decision on Ti-substitution of NMC-811 | Go/no go | Q4/no go decision made, because Ti substitution did not improve performance |

*We are in the process of transitioning from a project on Ni-rich NMCs to a new one involving emerging cathode materials. These milestones are for the NMC project.

# Milestones-FY2019

| Milestone | Type | Date/Status |
|---|---|---|
| Complete TXM Co K-edge experiments on NMC-811 system* | Milestone | Q1/Completed |
| Select materials that undergo O redox, determine synthesis routes | Milestone | Q2/Underway (as of March 2019) |
| Synthesis candidate materials, characterize | Milestone | Q3/Underway |
| Down-select materials based on properties | Go/no go | Q4/Planned |

* The first part of FY2019 is devoted to finishing the prior NMC project.

Any proposed future work is subject to change based on funding levels

# Milestones-FY2020

| Milestone | Type | Date/Status |
|---|---|---|
| Electrochemically characterize candidate materials and prepare samples for analysis | milestone | Q1/Planned |
| Start selected synchrotron experiments (XAS, XPS, TXM, XRS) | milestone | Q2/Planned |
| Go/no go decision on XRS | Go/no go | Q3/stop if requirement for large sample size is an impediment or if no useful information is obtained from O K-edge data |
| Select samples for STEM/EELS analysis | milestone | Q4/Planned |

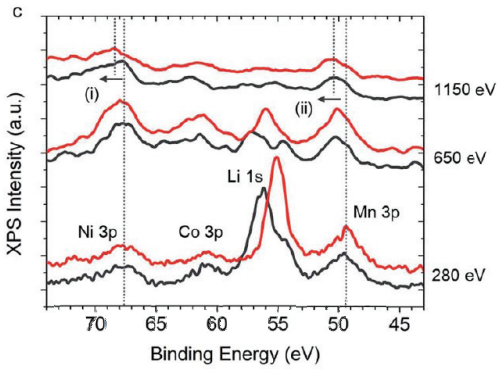
Any proposed future work is subject to change based on funding levels

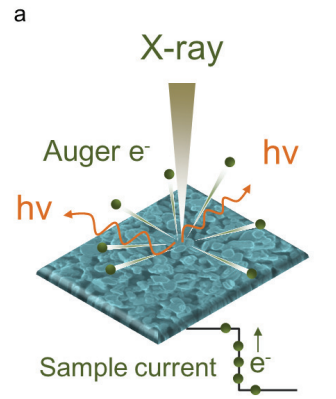
# Approach

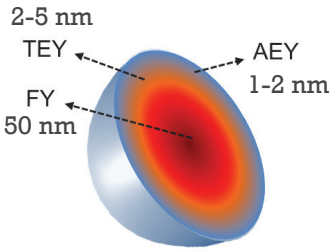
- We synthesize candidate cathode materials including NMCs and emerging cathode materials, using several different methods, and characterize them. For some experiments, we use commercial materials.
- We use an array of bulk and surface-sensitive synchrotron techniques to characterize cathode materials, including chemically and electrochemically delithiated samples
- Depending on technique, information needed, and time constraints, we may perform some of these experiments *in situ* or *ex situ.*
  - *Advantage to in situ experiments is that we can capture phenomena in real time. Disadvantages are the large amount of time they take, and the possibility that the experimental design is not relevant to the device.*
  - *Advantage to ex situ experiments is that many samples can be examined in a short amount of time, and the information then used to design in situ experiments. A disadvantage is that processing samples may compromise their integrity.*
  - *In situ experiments can provide information about a system undergoing dynamic changes, while ex situ ones probe an equilibrated system. Both types of information can be relevant.*

# Approach

hν=50-1500 eV
$E_{kin}$~100-1500 eV
$E_{kin}$ tunable for each core peak
Inelastic mean free path (IMFP) from <1 nm to several nm

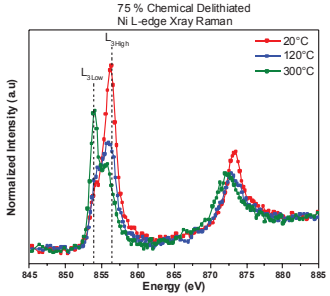


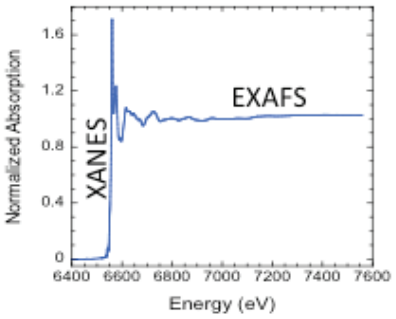




AEY- Auger Electron Yield
TEY- Total Electron Yield
FY- Fluorescence Yield

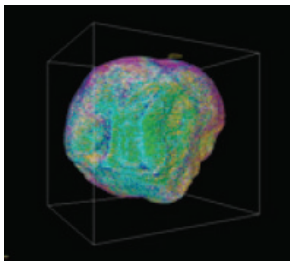
Soft XAS



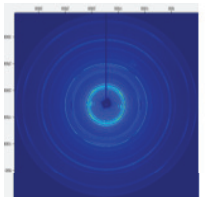

XRS-sensitivity of soft X-ray techniques, which probes mm deep.



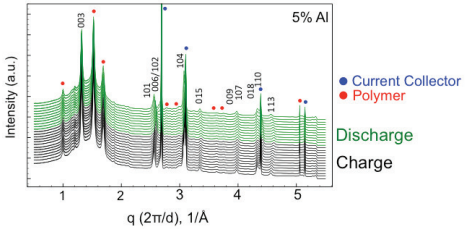

Hard XAS



TXM



2D diffraction image



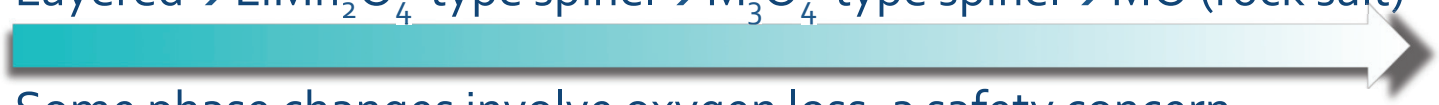

In situ XRD

Sub-nm — nm to tens of nms — bulk

Probing Depth

# Background

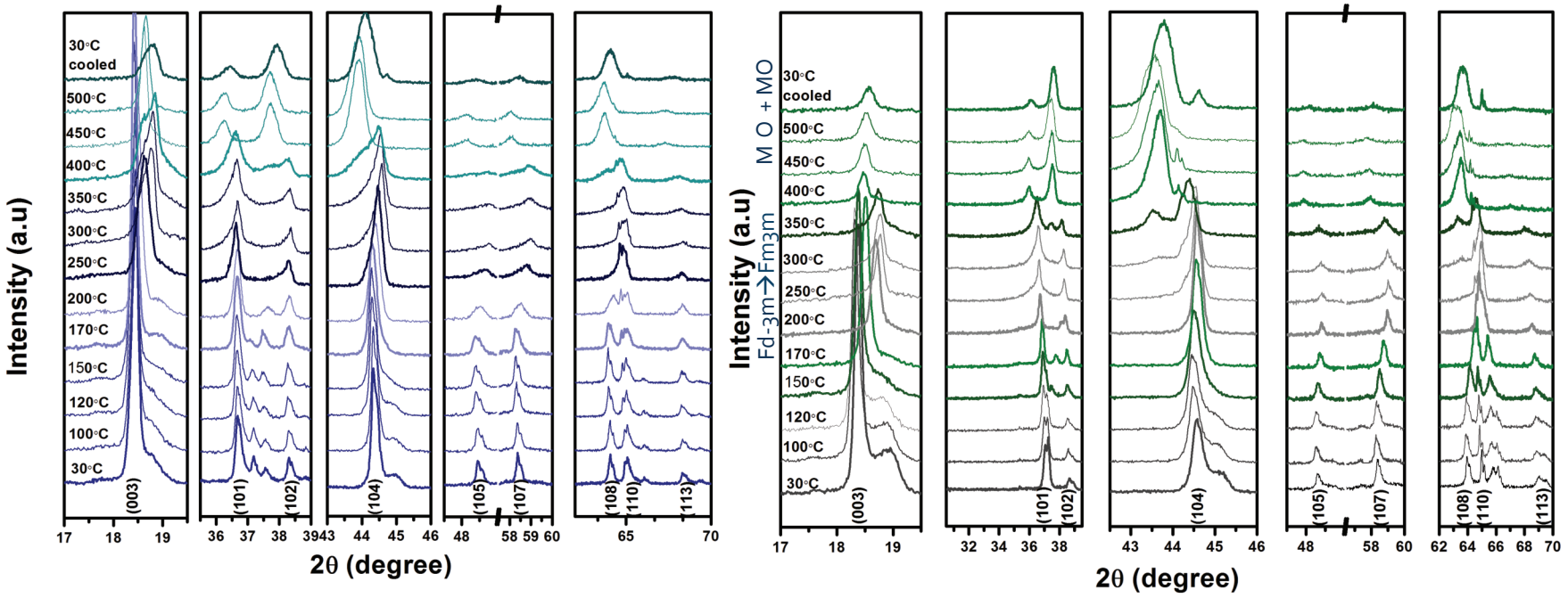
- Partially delithiated in house-made* NMC-622 and NMC-811 samples were prepared and heated to examine their thermal behavior. NMC-622 was completed last year, NMC-811 begun.
- NMCs undergo the following bulk phase changes
  - Layered→$LiMn_2O_4$-type spinel→$M_3O_4$-type spinel→MO (rock salt)



  - Some phase changes involve oxygen loss, a safety concern
  - The temperatures at which these transitions occur decrease with increasing Ni content and decreasing Li content. Changes can be seen in the bulk as low as 120°C for highly delithiated samples.
  - While these temperatures are not reached during normal operation, thermal runaway can occur under abuse conditions. Oxygen evolution exacerbates the thermal runaway and the threat of fire.

** By making samples ourselves, we can be sure that we have the desired composition and that they have not degraded. Commercial samples are not always the stated composition, and we cannot be sure that they have been stored properly.*

# Technical Accomplishments and Progress



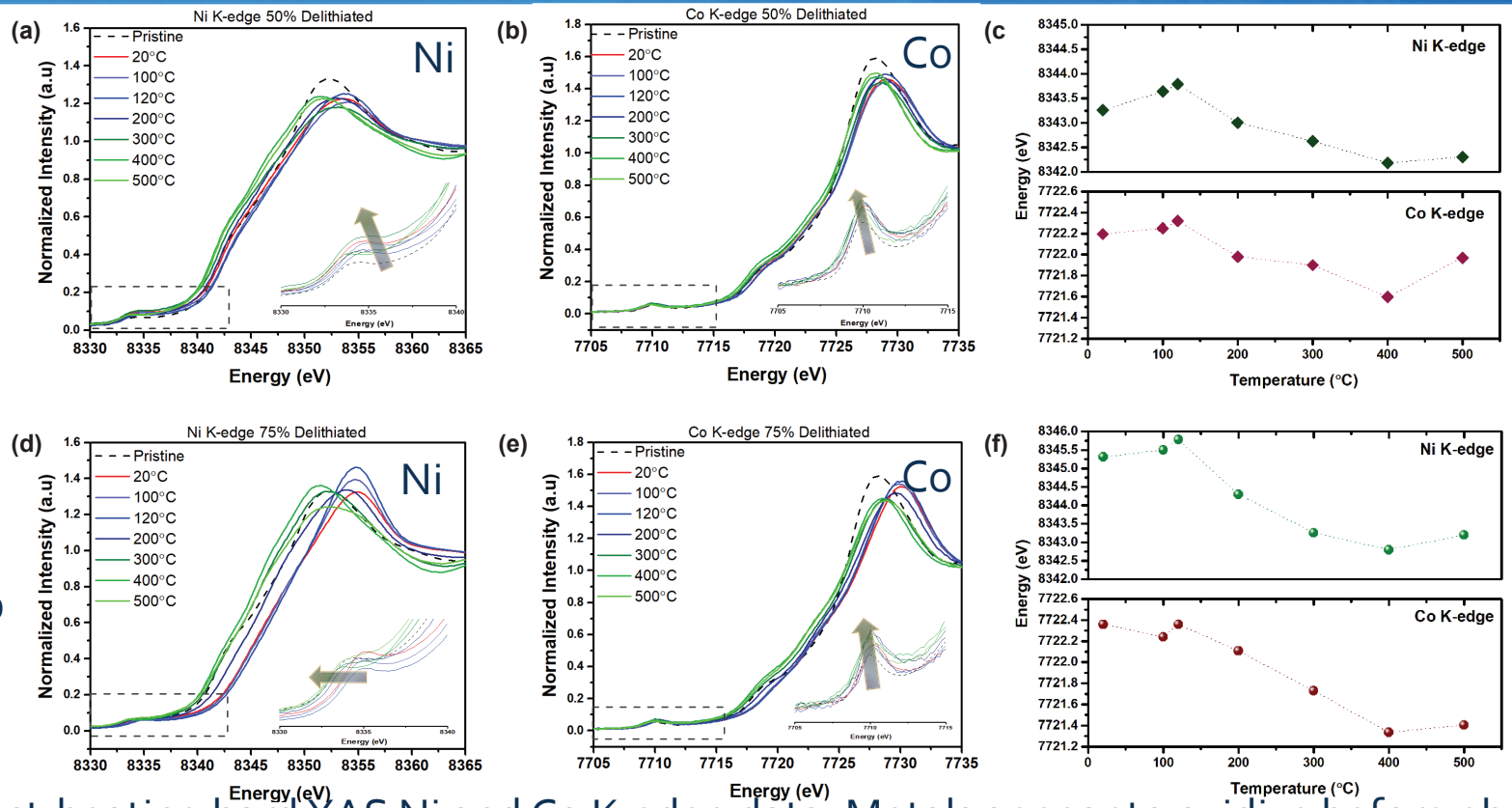

*In situ* XRD patterns of 50% and 75% delithiated NMC-811 undergoing heating in a lab diffractometer. Both materials are mixtures of H2 and H3 phases initially. The 50% delithiated sample converts primarily to spinel. The 75% delithiated sample converts to $M_3O_4$ and MO.

Note: this data was presented last year and is provided here for context

# Technical Accomplishments and Progress

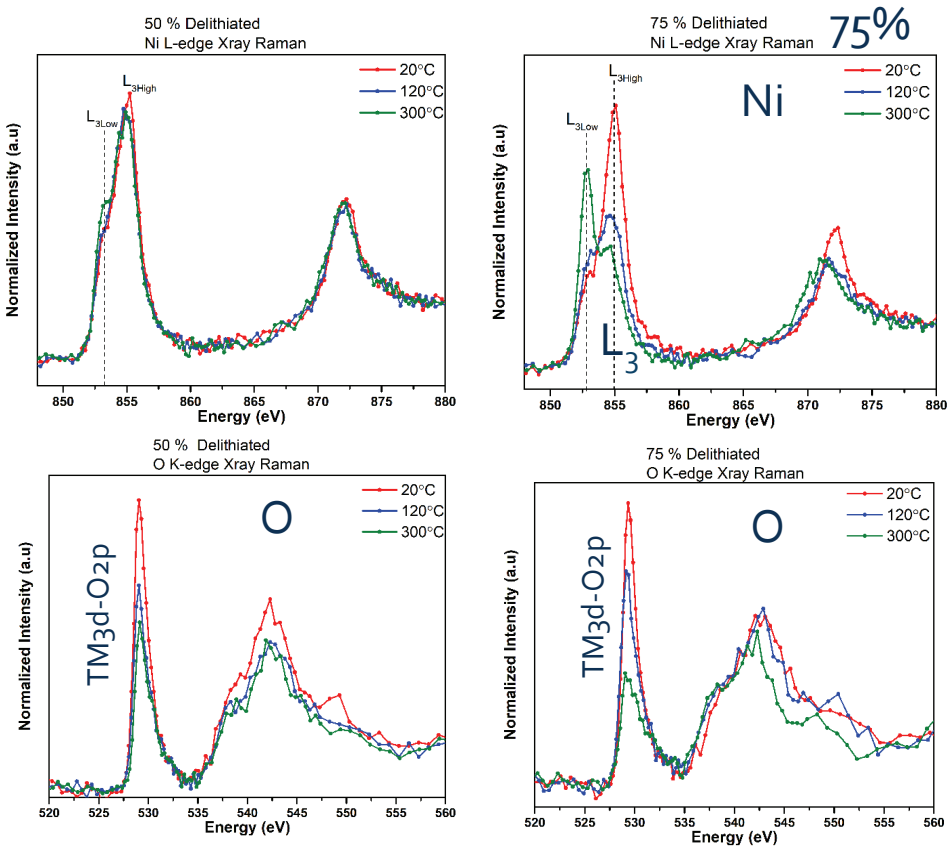
50%

75%



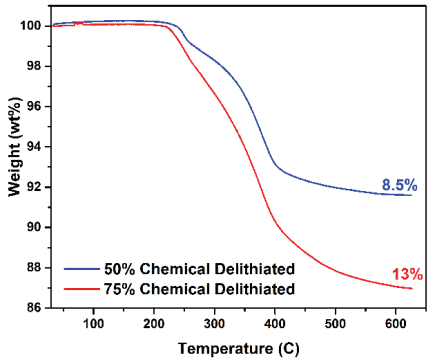

Post-heating hard XAS Ni and Co K-edge data. Metals appear to oxidize before phase changes occur (~100°C), then are reduced throughout the heating, consistent with phase changes. Intensification of Co pre-edge peaks as $M_3O_4$ spinel forms implies that Co occupies tetrahedral sites. No change in Mn redox state.

# Technical Accomplishments and Progress




In situ X-ray Raman Ni L-edge and O K-edge experiments as a function of temperature.

- Small amount of Ni reduction for 50% sample, more evident for 75% sample (oxidation not evident at 120°C), in situ experiment is on a different time scale than XAS).
- Decrease in intensity of TM3d-O2p peak in O K-edge spectra at 120°C, prior to O loss. Number of hole states on O decrease. Electron density moves away from the T.M. to O (change in covalency).

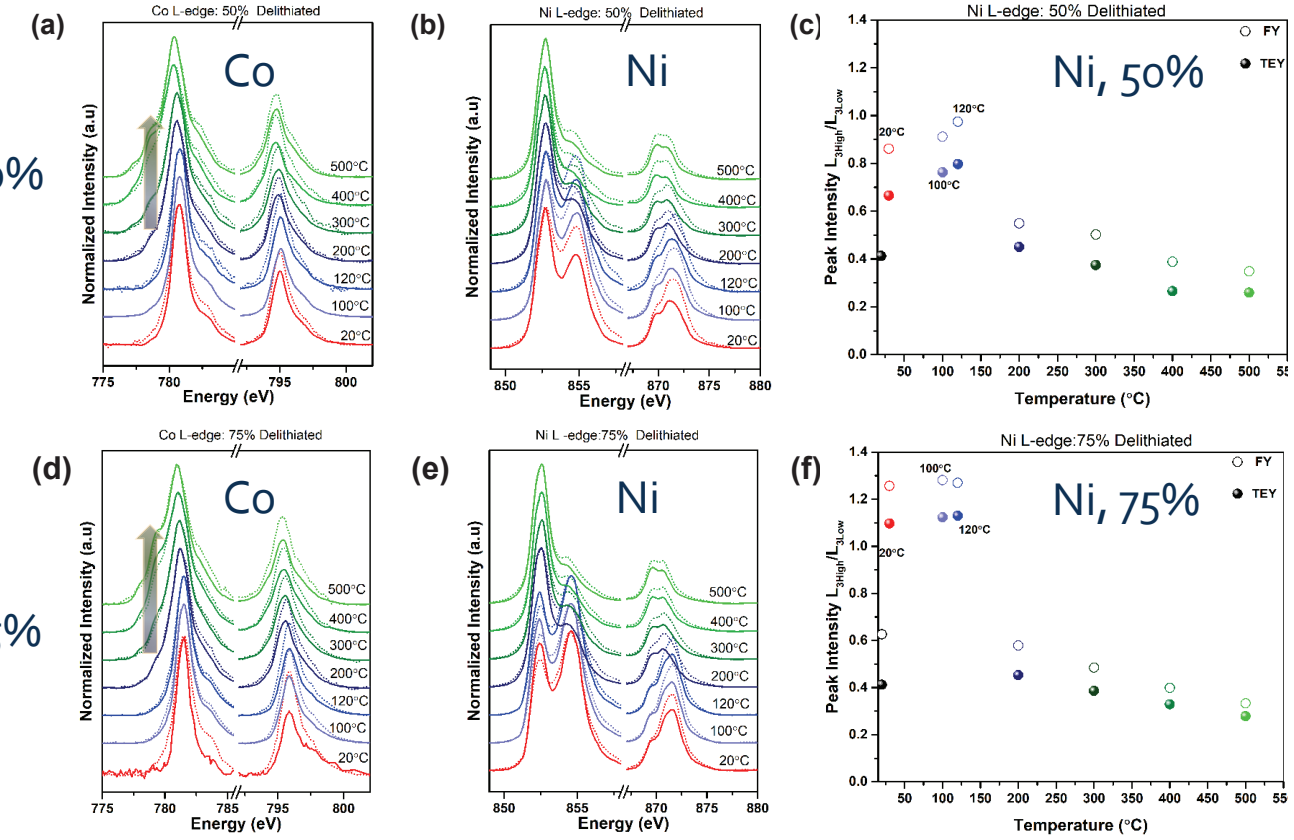



TGA data

# Technical Accomplishments and Progress

50%

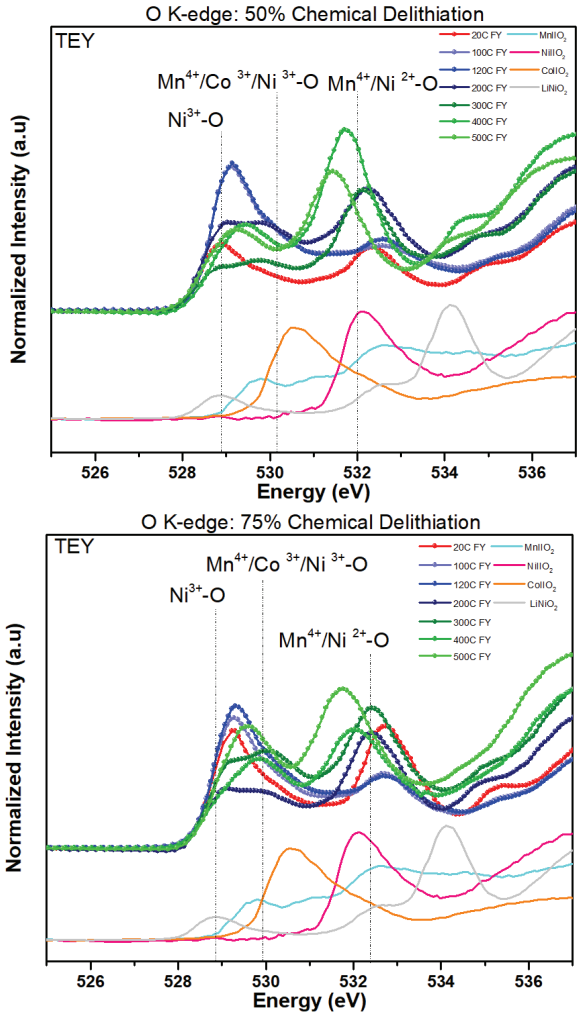
75%




- Similar to the hard XAS experiment, Ni and Co first oxidize, then reduce as the temperature increases.
- Surfaces are slightly more reduced than the bulk at all temperatures.

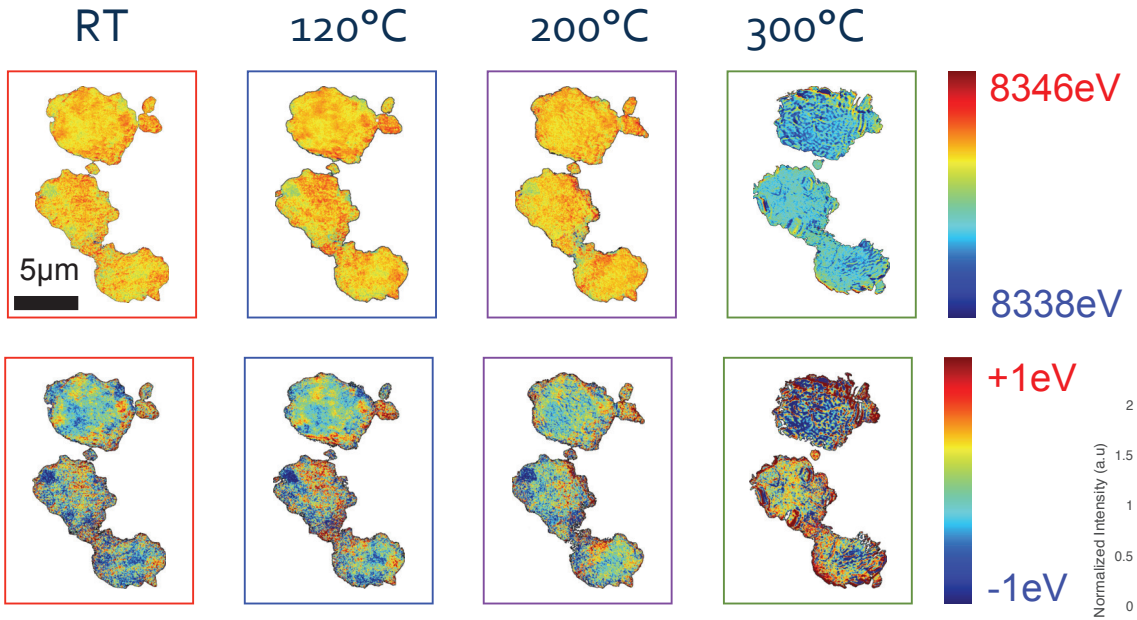
*Ex situ* Ni and Co L-edge XAS on heated samples

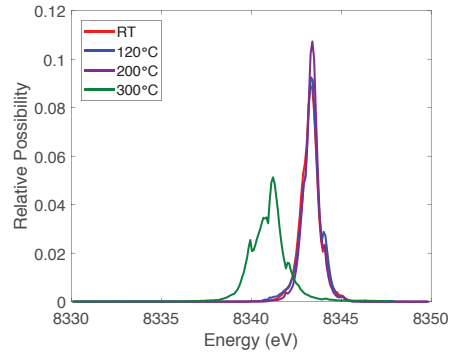
# Technical Accomplishments and Progress



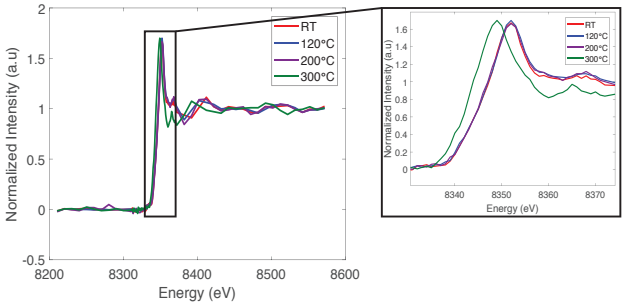

- In situ O K edge XAS data in TEY mode, showing TM3d-O2p region for 50% delithiated (top) and 75% delithiated (bottom) NMC-811 samples
- Ni at the surface first oxidizes near 120°C, then is reduced at higher temperatures, consistent with the Ni L-edge data.

# Technical Accomplishments and Progress



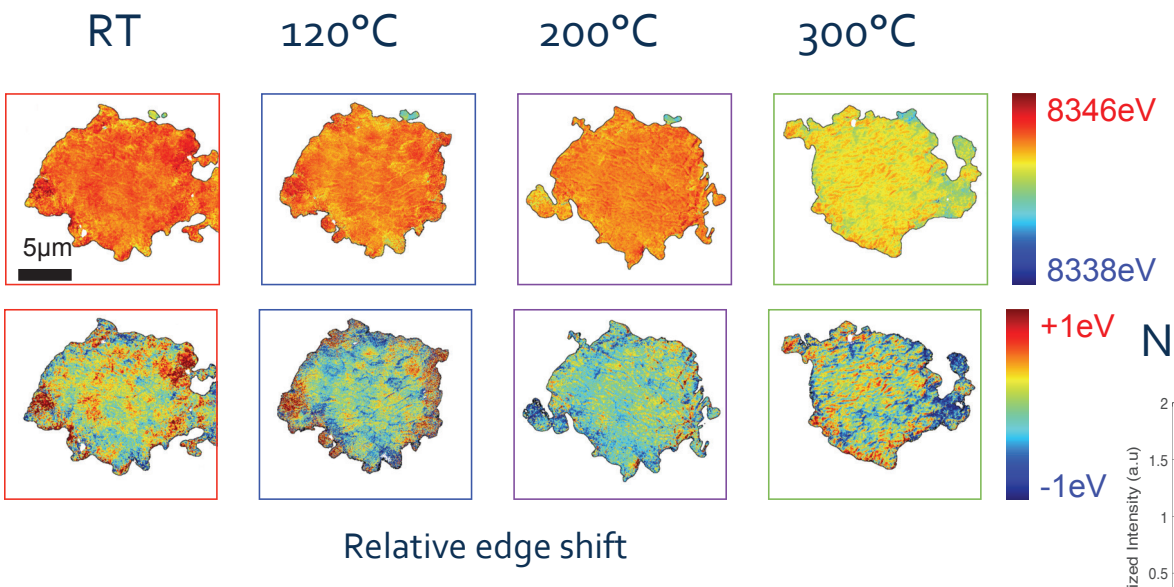



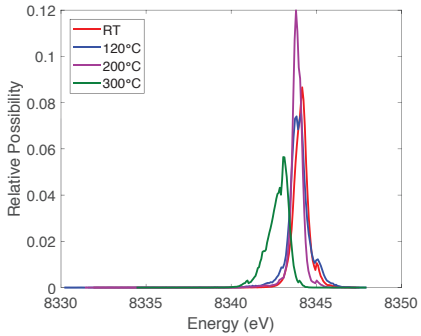

Ni K-edge energy distributions



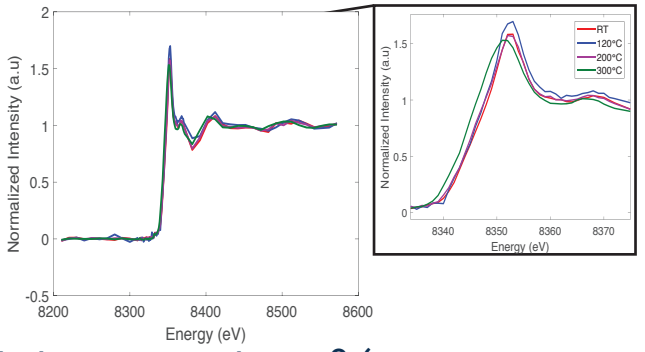

2D TXM images of 50% delithiated NMC particles heated in the beam line. There is a wide distribution of Ni oxidation states (upper right) in the particles even in the unheated material. Images show considerable heterogeneity at all temperatures. Significant reduction is seen at 300°C.

# Technical Accomplishments and Progress



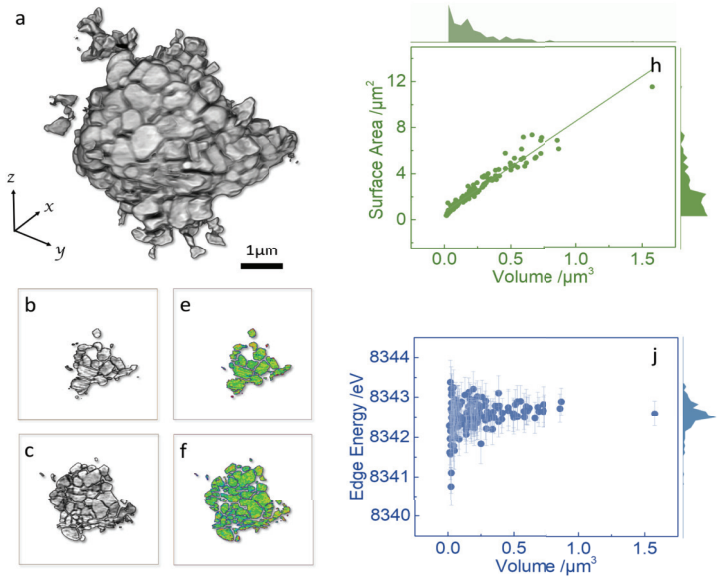




Ni K edge energy distributions

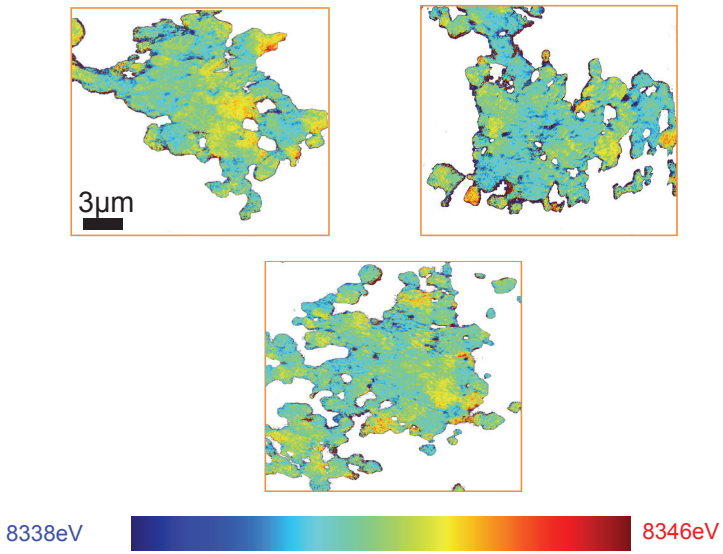



2D TXM images of a 75% delithiated NMC811 particle shows heterogeneity in Ni oxidation states both before and after heating. There are subtle changes in oxidation states even at 120° (some regions oxidize, others reduce). This implies movement of lithium ions. The particle changes shape, probably due to oxygen evolution associated with phase changes.

# Technical Accomplishments and Progress




a) 3D rendering of tomographic analysis. (b) and (c) virtual slices through different depths in the x-z plane, (e) and (f) are the corresponding XANES maps. (h) correlation analysis of the surface area and (j) Ni K-edge energy vs. primary particle volume.

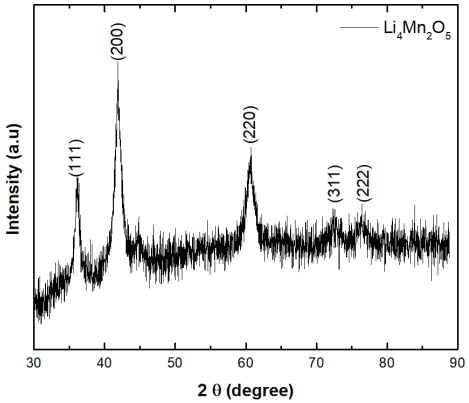



2D TXM showing maps of Ni K-edge energies. Considerable heterogeneity is evident in these samples after heating to 300°C.

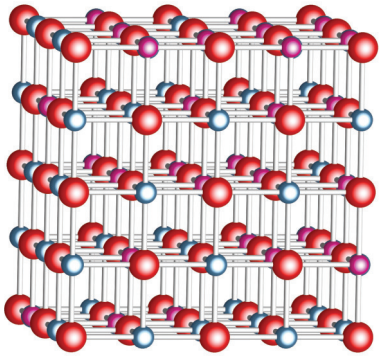
3D Ni XANES analysis of 75% delithiated NMC811 particles after heating to 300 °C. Average primary particle size is 1-1.5 µm, and smaller particles are more complex in shape. They are also more prone to reduction.

# Technical Accomplishments and Progress

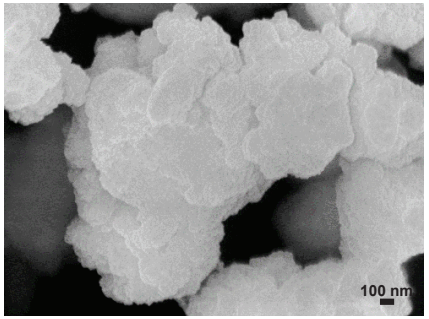
- New project-study interfacial properties of electrode materials that undergo O-redox.
- First material selected: $Li_4Mn_2O_5$, theoretical capacity 492 mAh/g, 355 mAh/g observed (Pralong et al., Nature Mater. 2015, 15, 173.)
- Synthesized by high energy milling of $LiMnO_2$ and $Li_2O$ (mechanochemical synthesis).




XRD pattern of $Li_4Mn_2O_5$ made in house



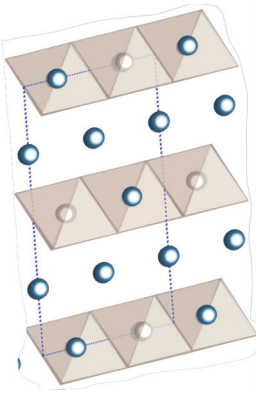
Rock salt structure of $Li_4Mn_2O_5$

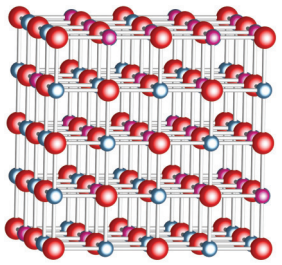


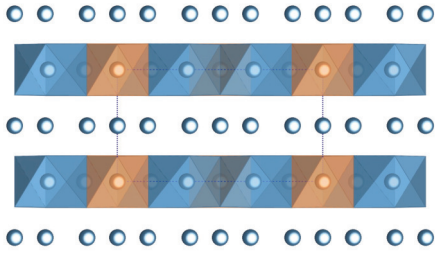

SEM image of $Li_4Mn_2O_5$

# Technical Accomplishments and Progress

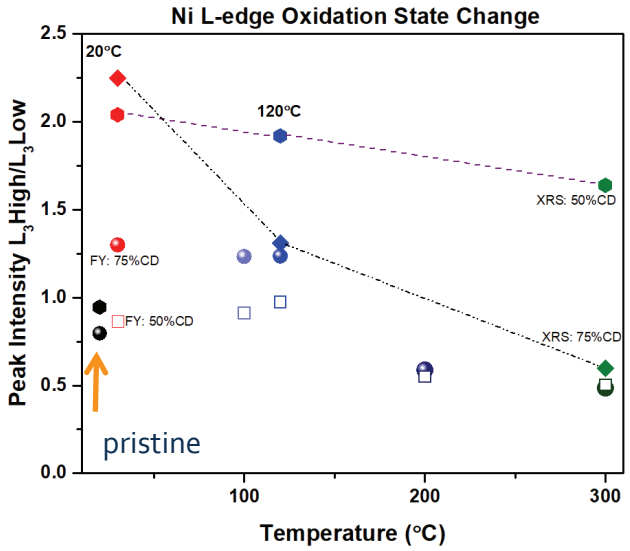
- Other materials selected
  - $Li_2Ru_xM_yO_3$; x+y=1, M=Sn, Fe, Ti
    - Sathiya et al., Nature Mater. 2013, 12, 827.
    - Up to 250 mAh/g, well-behaved cycling
  - β-$Li_2IrO_3$
    - Pearce et al. Nature Mater. 2017, 16, 580
    - Excellent cycling behavior but limited capacity
    - Model compound
  - $Li_4FeSbO_6$
    - McCalla et al., Chem. Mater. 2015, 27, 1699.
    - O and M redox happen simultaneously
    - High capacity, but poor cycling
  - Materials are selected based on differences in electrochemical behavior and structure.
  - We aim to study their behavior using depth-profiling techniques to understand these differences.

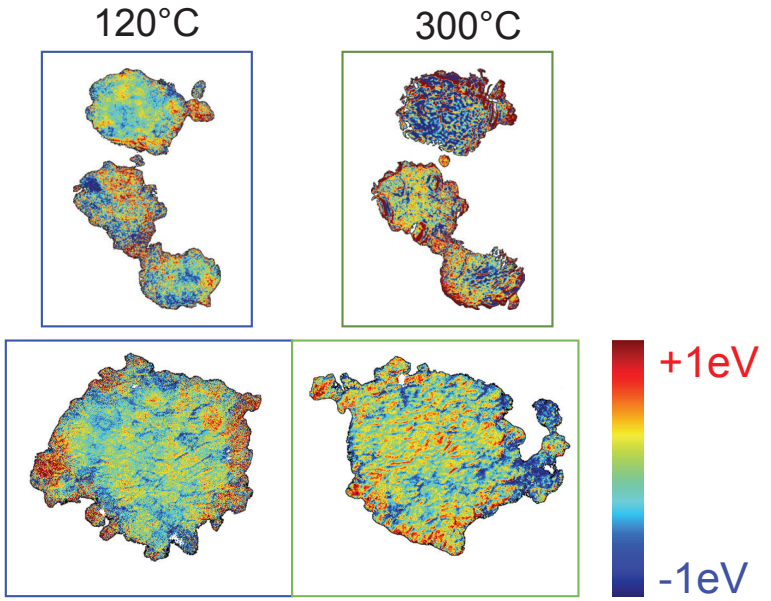


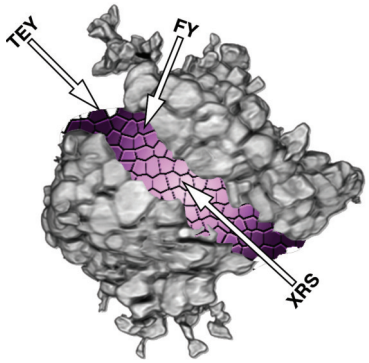




# Summary




An array of techniques, which probe to different depths, reveal considerable complexity in how NMC811 behaves thermally. There is considerable heterogeneity, with differences seen between surface and bulk, and dependent upon particle size and other factors.

# Summary

- XRD gives information about bulk transformations for partially delithiated NMC811 upon heating, but other techniques reveal more complexities in these processes.
- Ni and Co are reduced, but Mn is not.
- Apparent paradoxical oxidation of Ni at 100-120°C may simply reflect a change in covalency upon heating, but serves as a marker for phase changes.
- Reduction is highly heterogeneous, and differs on the surface from within the bulk. It is also dependent upon particle size and curvature (see our paper in **Nano Letters**, 10.1021/acs.nanolett.8b01036 (2018). )
- Results imply considerable mobility for Li at moderate temperatures and Ni at 300-350°C, which contributes to the heterogeneity that is observed.
- We are transitioning to a new project on emerging cathode materials that exhibit O-redox behavior. We have selected several candidates for study based on an array of electrochemical behaviors-some cycle well and others do not. Using techniques we have developed for the NMC work, we hope to gain an in-depth understanding of these materials, which can contribute to further development of high energy cathode materials.

# Collaboration and Coordination with Other Institutions

| Institution | Role | Comments |
|---|---|---|
| Stanford Synchrotron Radiation Lightsource (SSRL) (Yijin Liu, Dennis Nordlund, Chenxi Wei, Thomas Kroll, Dimosthenis Sokaris) | Synchrotron studies | We work closely with beam line scientists at SSRL to carry out cathode characterization work. |
| Bosch, NA (Saravannan Kuppan, Michael Metzger) | Collaboration on thermal studies on NCA | Several papers published or in the works. Bosch is no longer working on batteries. |
| Virginia Tech (Feng Lin) | Collaboration on thermal studies on NMCs | Our work with SSRL and VA Tech has been published recently. |

# Remaining Challenges and Barriers

- *Please note that this presentation was prepared in March, 2019.*
- We transitioned to a new project in FY2019 concerning O-redox materials. We spent Q1 finishing up our old project on Ni-rich NMCs with DOE's permission. This presentation mainly concerns the old project, because of this time line. We have started work on the new project.
- We rely on synchrotron facilities to do our work. Beam time is scheduled at set times by SSRL. It is subject to postponement in the case of equipment malfunction or maintenance.
- Earlier in the project, we did extensive electrochemical and physical characterization of NMCs and published on this work. In the interest of space, we cannot provide our conclusions here, but interested parties can consult our review, Acc. Chem. Res. 51, 89 (2018), for further details.
- We used chemically delithiated samples for this work, to avoid complications from other electrode components. We have published on the differences between chemically and electrochemically delithiated samples (Joule 2, 464 (2018), and have concluded that working on chemically delithiated samples is a valid approach for the reported work.

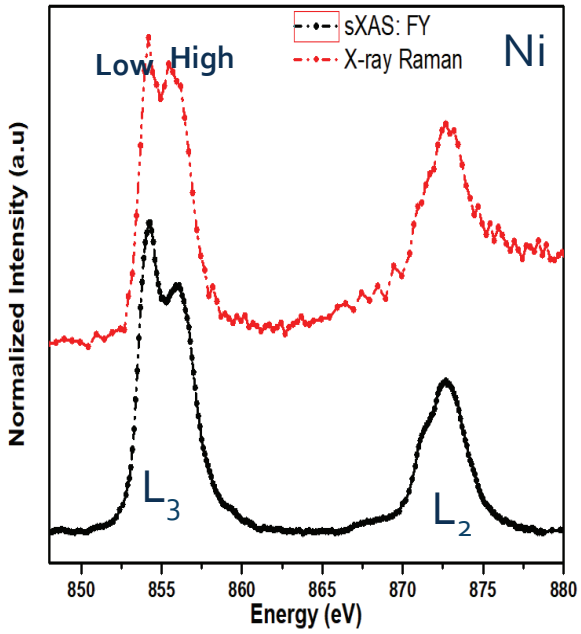
# Proposed Future Research

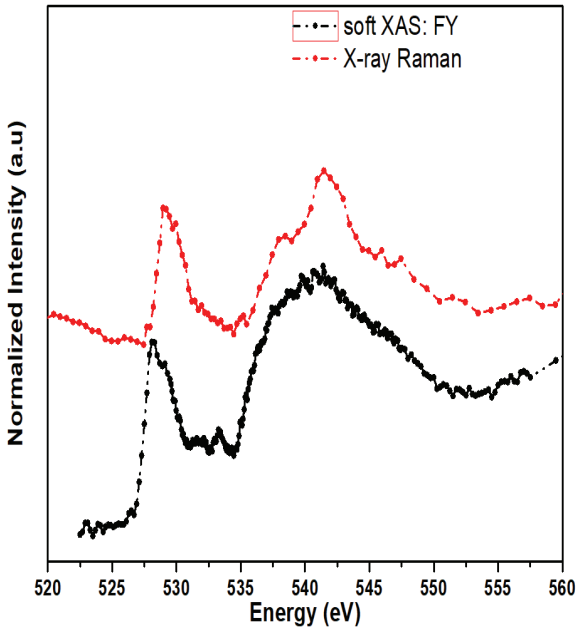
- We will synthesize candidate electrode materials exhibiting O-redox behavior, and characterize them electrochemically and physically. We have selected materials with different structures and behaviors (some cycle well and some don't), and have included model materials, as well as those that may have practical utility, but that don't yet cycle well.
- We will carry out *in situ* and *ex situ* depth-profiling experiments to understand the differences in O-redox behavior. Experiments will include pristine and cycled materials.
- An ultimate goal is to obtain insights that could help us develop practical high energy cathode materials.

Any proposed future work is subject to change based on funding levels

# Technical Backup Slides

# Bulk vs. Surface: X-ray Raman (XRS) and sXAS

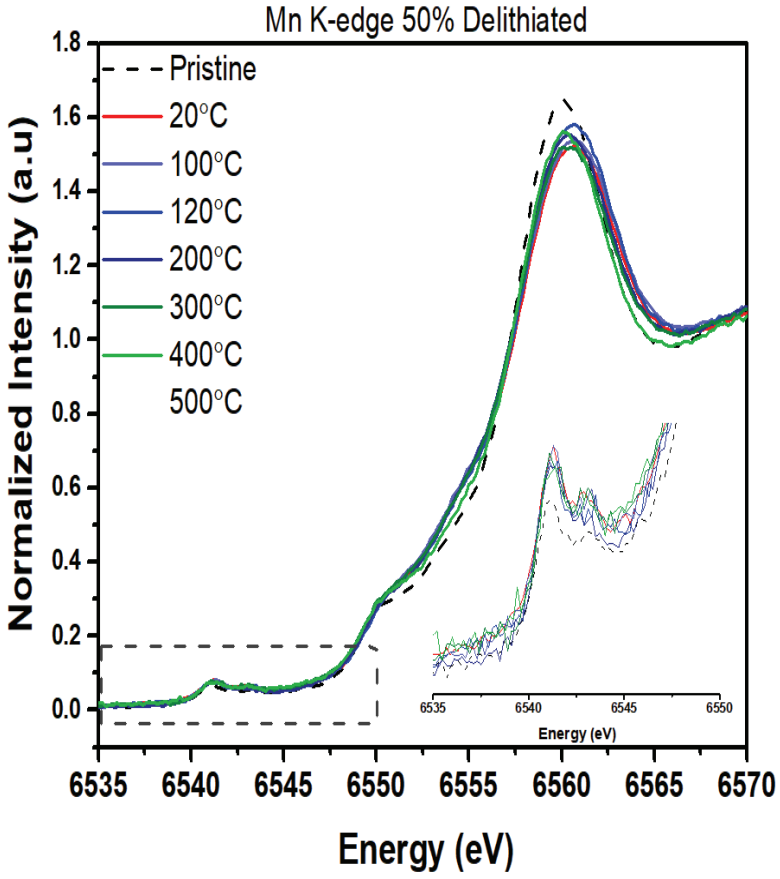


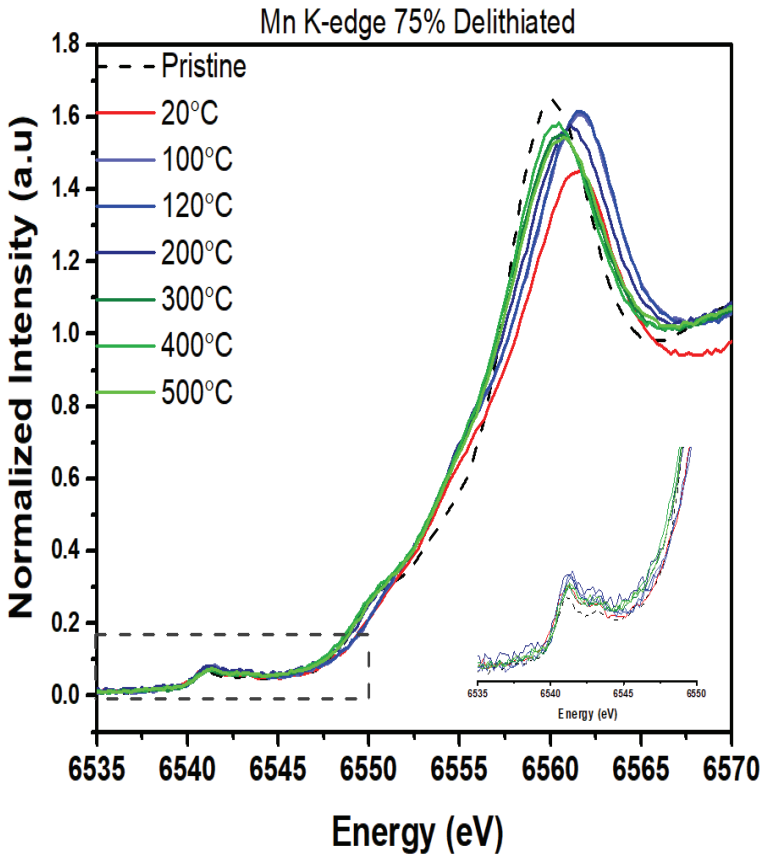




| Technique | $L_{3high}/L_{3low}$ | Probing depth |
|---|---|---|
| sXAS-FY | 0.79 | 50-100nm |
| XRS | 0.94 | mm (pellet) |

- Soft XAS and XRS yield qualitatively similar Ni L-edge and O K-edge spectra for pristine (as-made) NMC811.
- Differences can be attributed to the different probing depths, and the fact that samples are often reduced on the surface (surface reconstruction).

# Thermal Stability of Manganese

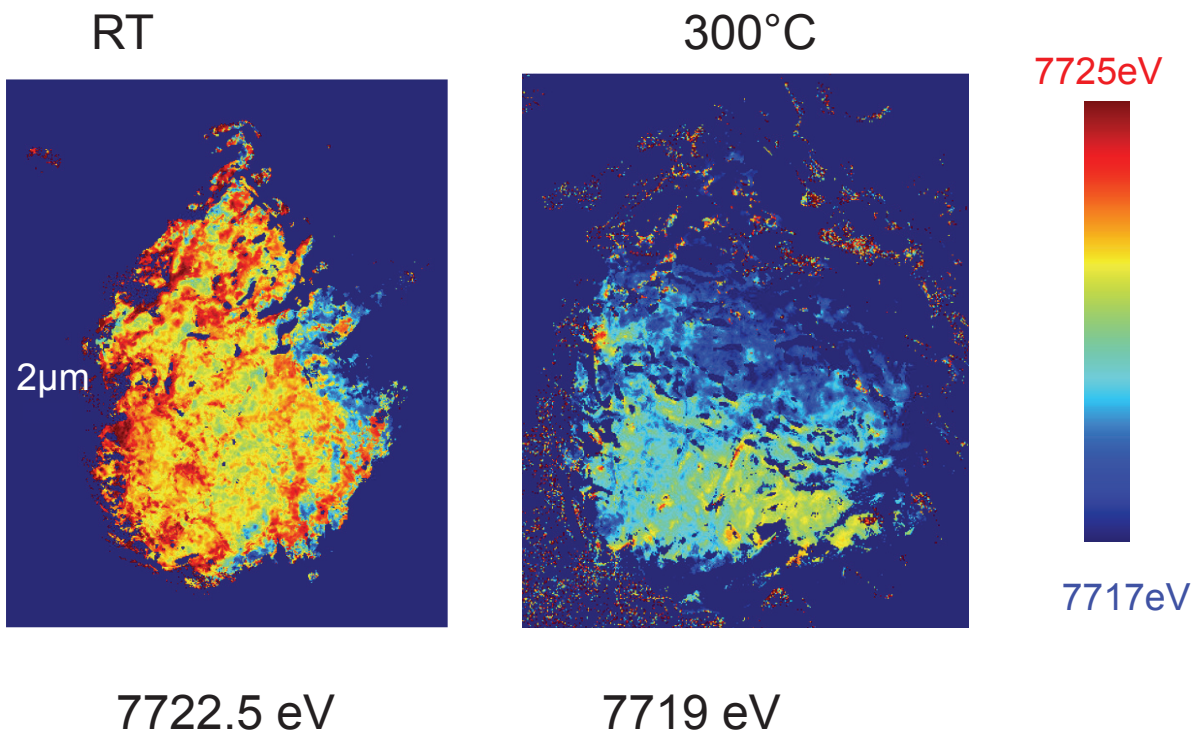



Hard XAS Mn K-edge data

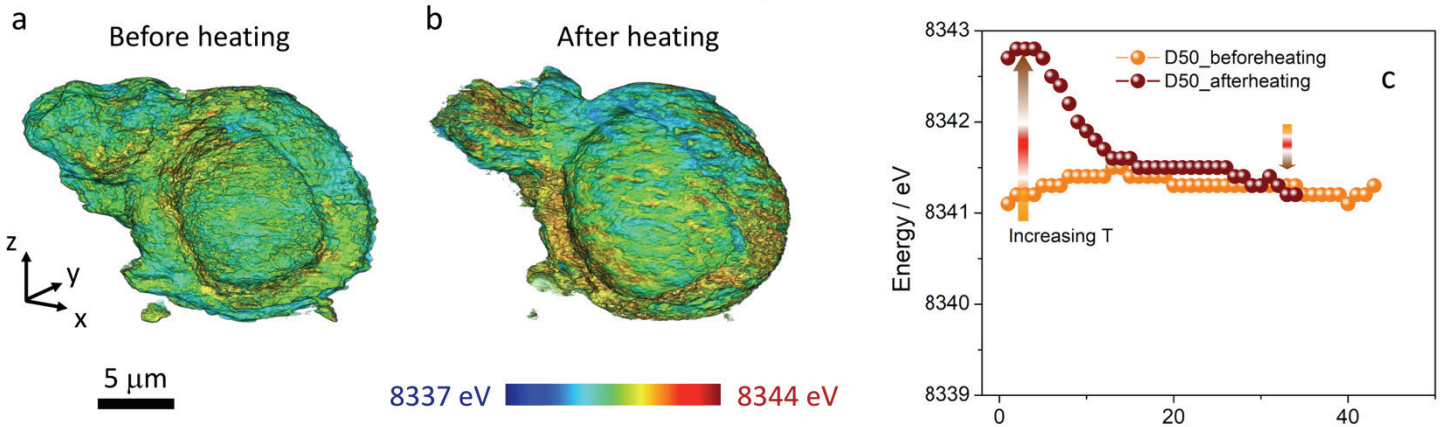
Little change is seen in Mn oxidation state after heating of samples.

# Co K-edge TXM mapping

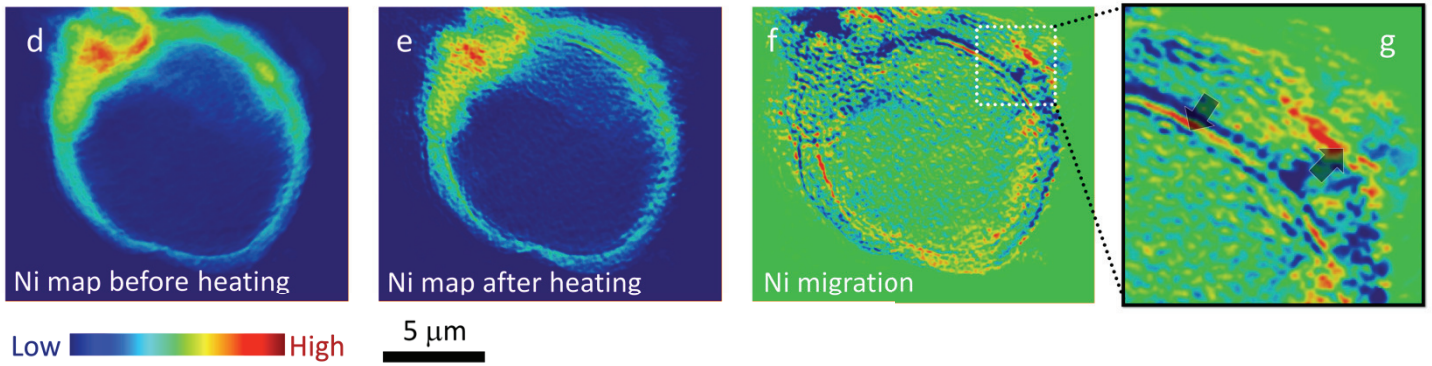



2D TXM images showing distributions of Co oxidation states in a 75% delithiated NMC-811 particle. There is considerable heterogeneity both at room temperature and at 300°C, but it is clear that Co is reduced significantly at 300°C.

# TXM mapping of Ni content in 50% delithiated NMC-622




Ni oxidation state distributions before and after heating to 350°C




Ni concentration, before and after heating  Ni concentration difference maps

Changes in Ni concentration (migration) upon heating contribute to oxidation state gradients

These experiments were done last year and are provided for context.